

ELECTRICALLY CONDUCTIVE POLYMERS

Field of the invention

The present invention relates to a method of preparing electrically
conductive polymeric material by treatment with a viologen salt and to electrically
conductive polymeric articles formed thereby.

Description of related art

In recent years electrically conductive polymers have been widely studied
because of their potential important commercial applications. Such polymers
include polypyrrole and its derivatives and polyaniline and its derivatives.

The aniline family of polymers is an example of one of the most widely
studied electroactive polymers because of the ease of synthesis and the unusual
nature of its electrical conductivity which can be varied over a wide range.
Polyaniline (PANi) in its insulating base form is readily soluble in N-
methylpyrrolidinone and can be cast into films or coated on different substrates.
The insulating form can be converted to the conductive form by the following
methods:

(1) Treatment with protonic acids

PANi in the emeraldine (50% oxidated) base state when treated with
protonic acids shows an increase in electrical conductivity. The resulting
conductivity is a strong function of the pH of the equilibrating solution. For
example, when aqueous HCl is used at pH greater than 4, the PANi remains as
the essentially insulating non-protonated form whereas at pH~0 (i.e. with 1 M
HCl), the conductivity increases by 10 orders of magnitude (J. C. Chiang and A.
G. MacDiarmid, *Synth. Met.* 13, 193 (1986)). In the latter case, the imine units of
the PANi are protonated to give a N^+/N ratio of about 0.5. In this form of doping,
there is no change in the number of electrons in the PANi chains.

The electrical conductivity of the PANi treated with protonic acids depends not only on the pH of the equilibrating solution but also on the oxidation states of the PANi. For example, PANi in the leucoemeraldine (100% reduced) state shows only a small increase in conductivity when treated with protonic acids (J. C. Chiang and A. G. MacDiarmid, *Synth. Met.* 13, 193 (1986)).

(2) Charge transfer interaction with organic electron acceptors

PANi in the emeraldine base state can undergo charge transfer interaction with organic electron acceptors such as tetrachloro-o-benzoquinone and 2,3-dichloro-5,6-dicyano-p-benzoquinone in acetonitrile (S. H. Khor, K. G. Neoh and E. T. Kang, *J. Appl. Polym. Sci.* 40, 2015 (1990)). An increase in electrical conductivity is achieved and the magnitude of the conductivity is dependent on the type of organic acceptors and acceptor concentration. The charge transfer interaction of emeraldine base with the organic electron acceptor is analogous to that of protonation by HCl, with the hydrogen atoms in the latter replaced by the partially dehalogenated halobenquinone rings. The maximum conductivity achieved is at least an order of magnitude lower than that achievable in protonic acid doping of emeraldine base.

PANi in the leucoemeraldine state undergoes oxidative doping by organic electron acceptors in acetonitrile solution which involves first the oxidation of the amine nitrogen and also the formation of the imine structure through hydrogen transfer from the amine nitrogen to the acceptor. The so-produced imine nitrogen is then in turn doped by the acceptor, as described above for PANi in the emeraldine state (E. T. Kang, K. G. Neoh, T. C. Tan, S. H. Khor, and K. L. Tan, *Macromolecules.* 23, 2918 (1990)). The maximum electrical conductivity obtained is also about an order of magnitude lower than that obtained from protonic acid doping of emeraldine.

It would be a significant advance in the art if a method of preparing an electrically conductive polyaniline material could be provided which would function irrespective of the oxidation state of the polyaniline. The polyaniline base material

may be a substituted or unsubstituted polyaniline. It would be a further significant advance in the art if a method could be provided which did not involve the use of acid or organic solvents such as acetonitrile.

5 It is accordingly an object of the present invention to overcome, or at least alleviate, one or more of the difficulties and deficiencies related to the prior art.

Summary of the invention

Accordingly, in a first aspect of the present invention there is provided an electrically conductive polymeric article including a polymeric material capable of exhibiting electrical conductivity;

10 the polymeric material being rendered electrically conductive by treatment with a viologen salt.

15 It has surprisingly been found that the electrically conductive polymeric article according to this aspect of the present invention exhibits a high level of electrical conductivity. For example, electrically conductive polyaniline may be prepared with resistances (R_s) decreasing from approximately 10^{10} to approximately $10^6 \Omega/\text{sq}$ or below, irrespective of the oxidation state of the polyaniline material. Polyaniline material may be in the leucoemeraldine (0% oxidation state) or emeraldine (50% oxidation state) states or in any oxidation state between these two states.

20 Examples of polymeric materials capable of being rendered electrically conductive by treatment with a viologen include polymers derived from aromatic bases such as aniline and its derivatives and from heterocyclic bases such as pyrrole and its derivatives.

25 Prepared polymeric materials for inclusion in the polymeric articles of the invention include polyaniline and its derivatives and polypyrrole and its derivatives. Polyaniline and polypyrrole are particularly preferred polymeric materials.

The electrically conductive polymeric material may be formed in any suitable manner and may take any suitable shape. The polymeric may be in the form of a film, e.g. a free standing film, a film coating, e.g. a thin film coating, or a powder.

- 5 In a preferred aspect the polymeric material may be deposited or supported on a suitable substrate. The substrate may be a fabric, polymeric matrix film or other construct. A polyethylene substrate, e.g. a low density polyethylene (LDPE) substrate may be used.

10 The viologen salt utilised to dope the polymeric material may be of any suitable type. Viologen salts such as a dihalide salt of a viologen (1,1'-disubstituted 4,4'-bipyridinium dihalide) have been found to be particularly suitable.

15 The substituents on the bipyridinium molecule may be selected from alkyl or aryl groups. The alkyl groups may be substituted or unsubstituted C1 to C4 alkyl groups. The alkyl groups may be straight or branched chains. Substituents for the alkyl groups may be selected from a wide range of substituents including halogen, phenyl and substituted phenyl. Examples of preferred alkyl groups include methyl, ethyl, propyl, butyl and phenylmethyl (benzyl). The aryl groups may be substituted or unsubstituted aryl or heteroaryl.

- 20 Viologen salts may be provided as free compounds, shown below as I, or in the form of polymers, shown below as II, where:

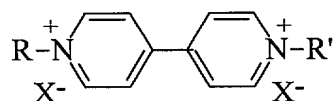
R and R¹ are independently chosen from alkyl or aryl groups as indicated above;

R² is an alkylene group, preferably a C₂ to C₄ alkylene group;

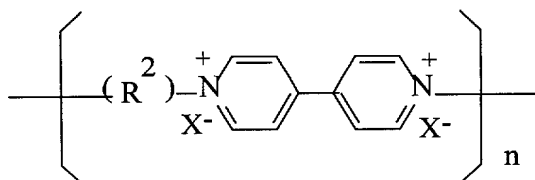
- 25 X⁻ is an anion, preferably a halide ion; and

n is an integer greater than or equal to 2.

Particularly preferred viologens include ethyl viologen dichloride, benzyl viologen dichloride and poly(butyl viologen dibromide).



(I)



(II)

In a preferred aspect of the present invention the polymeric material may be directly treated with a viologen to render it electrically conductive.

Accordingly, in a preferred aspect of the present invention there is provided a method of preparing an electrically conductive polymeric article, which method includes providing

a polymeric material capable of exhibiting electrical conductivity; and
a viologen;

contacting a surface of the polymeric material with the viologen for a time sufficient to permit the polymeric material to be rendered electrically conductive.

Although not wishing to be bound by theory it is believed that when the polymeric material is treated with a viologen salt that the polymeric material undergoes oxidative doping and the halide anions are incorporated into the polymer. Surprisingly the method may be conducted at or above room

temperature in the presence of air and preferably utilising an aqueous solution of the viologen salt. Thus the use of protonic acids or organic solvents may be avoided.

5 The rate of the reaction is dependent on the ease of the reduction of the viologen, e.g. a viologen dication, and the transfer of the anions to the polymeric material to form a doped and conductive form of the polymeric material.

10 Pursuant to the present invention, the reactions may be carried out by contacting the surface of the polymeric material with an aqueous solution of viologen salt. The reactions may continue for a time sufficient to permit a substantial degree of oxidative doping of the polymeric material to be achieved.

The viologen salt may be selected from any suitable materials as discussed above. A viologen dihalide is preferred.

15 The method of contacting the surfaces of the polymeric material with the viologen may vary widely, depending on the state of the polymeric material and the method selected for the reactions. One simple and preferred method involves immersing the polymeric material in an aqueous solution of the viologen salt, preferably a viologen dihalide, more preferably in excess, with proper agitation. The preferred concentration of the solution is between 0.01 M and 0.5 M.

20 The method may be conducted at any suitable temperature, e.g. at a temperature between 0° and approximately 100°C. The method may be conducted in the presence of air and under ordinary room lighting.

25 The method may be carried out for a period of time which is dependent on the form of the polymeric material (coating, thick film or powder), type of viologen salt and concentration. For example, for a thin PANi coating and a monomeric viologen dichloride at a concentration of 0.1 M, the reaction is rapid and the film turns conductive within 5 mins. For thick PANi films, and using a similar viologen type and concentration, the period of the experiment is extended to 1 day to

ensure completion.

After completion of the reaction, the polymeric material may, for example, be blotted dry between filter paper to remove the unreacted viologen salt. The change of the PANi from the insulating base state (brown and blue for emeraldine freestanding film and coating, respectively) to the conductive state (blue and green for freestanding film and coating, respectively) is visually apparent, and may be confirmed by sheet resistance (R_s) measurement, X-ray photoelectron spectroscopy or UV-visible absorption spectroscopy.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the sheet resistance (R_s in $\Omega/\text{sq.}$) versus time of emeraldine base free standing film treated in 0.24 M benzylviologen dichloride. Figure 2 shows UV-visible absorption spectra of PANi coating on LDPE film treated in 0.024 M polybutylviologen dibromide.

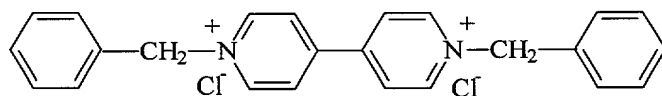
EXAMPLES

The following specific examples are provided to illustrate this invention and the manner in which it may be carried out. It will be understood, however, that the specific details given in each example have been selected for the purpose of illustration, and are not to be construed as being limitations on the scope of the invention.

EXAMPLE 1

Polyaniline (in the emeraldine or 50% oxidation state) was synthesized via the oxidative polymerization of aniline using ammonium persulfate in 0.5 M H_2SO_4 (A.G. MacDiarmid et al. *Synth. Met.* 18, 285 (1987)). The polyaniline powder was undoped using excess 0.5 M NaOH and the polyaniline (emeraldine) base powder was dissolved in N-methyl pyrrolidinone (NMP). Freestanding film of 10-20 μm was cast from the polyaniline base (8% wt) in NMP solution. This film was

immersed in a 0.24 M solution of benzyl viologen dichloride

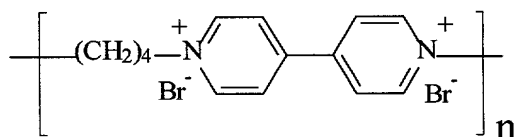


in water. The pH of the solution was between 5 and 6 and the experiment was carried out at 25 °C in an open test tube. A sharp decrease in R_s was observed within the first hour. The change in R_s with time of treatment is shown in Figure 1.

The doping level as given by the N^+/N ratio obtained is 0.4 after 24 h.

EXAMPLE 2

A coating of polyaniline (in the emeraldine state) on low density polyethylene (LDPE) substrate was prepared by immersing a O_2 plasma pretreated LDPE film into a reaction mixture containing 0.10 M aniline and 0.025 M ammonium persulfate in 0.5 M H_2SO_4 for 2 h. The green polyaniline coated LDPE film was undoped in 0.5 M NaOH for 2 h and then washed with deionized water and pumped dry under reduced pressure. The base film was immersed in a 0.024 M poly(butylviologen dibromide)



solution in water under ordinary room lighting. The change in the UV-visible absorption spectrum from that of emeraldine base to a conductive salt is illustrated in Figure 2.

EXAMPLE 3

Polyaniline freestanding (emeraldine) base film was synthesized as described in Example 1. Leucoemeraldine was prepared by treating the

emeraldine base film with 10% hydrazine for 48 h. After treatment of the leucoemeraldine film (pale brown) with 0.12 M benzyl viologen dichloride at 25 °C and under ordinary room lighting for 24 h, the film has turned blue and R_s decreased from 10^{10} to $6 \times 10^5 \Omega/\text{sq}$.

EXAMPLE 4

Polyaniline freestanding (emeraldine) base film was synthesized as described in Example 1. Treatment of the film with 0.12 M benzyl viologen dichloride at 5 °C was carried out for 24 h under ordinary room lighting. The R_s obtained was $3 \times 10^5 \Omega/\text{sq}$.

EXAMPLE 5

Polyaniline freestanding (emeraldine) base film was synthesized as described in Example 1. Treatment of the film with 0.12 M benzyl viologen dichloride at 25 °C was carried out for 24 h in the absence of light. The R_s obtained was $4 \times 10^5 \Omega/\text{sq}$.

EXAMPLE 6

Polypyrrole (PPY) freestanding film was electrochemically synthesized in a one-compartment cell with 0.1 M pyrrole, 0.1 M p-toluenesulfonic acid in acetonitrile containing 1% v/v water. The film was grown with a charge density of 10 Coulomb cm^{-2} at 0~5° C (X. Zhang, E. T. Kang, K. G. Neoh, K. L. Tan, D. Y. Kim and C. Y. Kim, *J. Appl. Polym. Sci.* 60, 1996, 625). The PPY film was then undoped by treatment in 0.5M NaOH for 24h. This dried PPY film was immersed in 0.24 M aqueous solution of benzyl viologen dichloride for 24h at 25°C under ordinary room lighting. The film turned dark blue and R_s decreased from 10^7 to $10^4 \Omega/\text{sq}$.

Finally, it is to be understood that various alterations, modifications and/or additions may be made without departing from the spirit of the present invention as outlined herein.

100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000